



# Top-down and facet-selective phase-segregation to construct concave nanocages with strongly coupled hetero-interface for oxygen evolution reaction

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## ABSTRACT

In this study, a top-down and site-selective anion etching method is devised to stepwisely carve out the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> concave hetero-cages (CHCs) from NiCo Prussian blue analogue (PBA) cube. DFT calculation investigates that the synthetic mechanism is based on anisotropic reactivity of each etchant acted in different facets of NiCo PBA cube and can be generalized to various heterogeneous combinations by tuning their dissolution and reconstitution kinetics (i.e. NiCoB/NiS<sub>2</sub>, NiCoP/NiS<sub>2</sub>). Such strategy without adding extra metal source generates strongly coupled heterointerface with hollow, concave, and ultrathin (~16.2 nm) features, which could harvest abundant active sites, tune the electronic structure, and induce strong lattice strain of Ni. Specifically, the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs manifest superior activity and stability toward oxygen evolution reaction (OER), with an overpotential of 258.0 mV required for 10.0 mA cm<sup>-2</sup>, a Tafel slope of 38.3 mV dec<sup>-1</sup>, and favorable long-term durability in 1.0 M KOH.

## 1. Introduction

Oxygen evolution reaction (OER) is one of the pivotal electrocatalytic processes in various electrochemical conversion systems (i.e. water splitting units, metal-air batteries), which requires lower activation energy and faster conversion kinetics to achieve maximized power output [1–6]. Developing non-precious-metal-based compounds with controlled architectures and chemical compositions has emerged as a cost-effective way to acquire highly efficient electro-catalysts for OER [7–11]. Metal-organic frameworks (MOFs) have been demonstrated as universal precursors for the fabrication of well-defined OER catalysts owing to their topology-transformable architecture and flexible component adjustability [12–15]. Starting from a MOF, there are two documented strategies to further optimize the conductivity, alter the adsorption behavior, and enhance the intrinsic activity: (i) cation regulation (Co<sup>3+</sup>, Ni<sup>2+</sup>, Mo<sup>2+</sup>), including seed-mediated growth to deposit new metallic compound on a MOF, or cation exchange reaction to carve the skin of a MOF ([M(CN)<sub>6</sub>]<sup>3-</sup>, MO<sub>3</sub><sup>2-</sup>) [16–18]. Thereby hetero-interfaces could be obtained to invoke synergistic effects of electronic interactions and interface reconstitution [19]. (ii) anion regulation (S<sup>2-</sup>, N<sup>3-</sup>, Se<sup>2-</sup>, OH<sup>-</sup>, etc.), which takes a top-down etching process involves the

breaking of metal/organic linkers and regrowth of covalent bonds to topologically convert MOF into well-structured compound with tailored intrinsic activity [20–23]. Generally, it often leads to highly open structures with enhanced atomic efficiency and shorter diffusion length for charge transport [24,25]. More important, anion etching method no longer introduces any additional metal source, which could fully motivate the utilization of internal metal sites of MOF noumenon, meanwhile accelerate the gas diffusion, electrolyte permeation, and reactants transportation for electro-catalysis [26].

Significant breakthroughs have been achieved on MOF-derived compounds by anion etching, showing specific geometric configurations (e.g. nanoframes, nanocages of single or multiple shells, yolk-shell) [27–31]. However, although the structural complexity have been realized, most of them are homogeneous compounds with single-phase composition (hydroxide, sulfide, phosphide, etc.) because the underlying anion etching process is straightforward and exhaustive [32]. Current study on selective anion etching can only leave behind the initial MOF residua as a constituent part of the resultant heterostructures, which is insufficient to act as highly active component for OER [33,34]. Accordingly, it is still difficult to solely using the anion etching for constructing component-heterogeneous MOF derivatives, due to the

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lack of systematic study on the etching rate/position/degree of each anion etchant acted in MOF [35]. Although it has been well recognized that the heterogeneous interface is favorable for OER, which could induce the subtle lattice distortion, modulate the charge separation and migration, and tailor the d-band center of metal sites at the Fermi level [36–38]. Furthermore, since the exquisite superstructures (*i.e.* concave, specific facets) with preferential reactivity are highly desirable for tailoring the intrinsic activity for OER [39,40], on above basis to endow the heterogeneous structure with specific spatial distributions and geometrical architecture is deserved, which could learnt from the success of the precise facets control of noble metal nanocrystals [41].

Herein, we demonstrate a two-step and facet-selective anion etching to construct the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> concave hetero-cages (CHCs) by kinetically controlling the anisotropic reactivity of each etchant acted in *fcc*-structured NiCo PBA nanocubes. NiCo PBA, a typical MOF, was selected as precursor due to its controllable structure and flexible component adjustability [42,43]. Firstly, an incomplete anion etching by S<sup>2-</sup> ions is used to preferentially carve the edges and corners of NiCo PBA, forming the NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes. Secondly, the internal PBA cross undergoes second anion etching by OH<sup>-</sup> to form the ultrathin NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs (forming the NiCoB/NiS<sub>2</sub> CHCs by BO<sub>2</sub><sup>-</sup> etching and forming the NiCoP/NiS<sub>2</sub> cross@frame heterocubes by PO<sub>4</sub><sup>3-</sup> etching). Such strategy could avoid the addition of extra metal source, thus endows the products with hollow, concave, and ultrathin (~16.2 nm) features. Meanwhile, EXAFS analysis investigates that the strongly coupled NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> heterointerface could increase the lattice disorder, tune the electronic structure, and induce the strong lattice strain of Ni. Inspired by above merits, the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs manifest superior activity and stability towards OER in alkaline medium.

## 2. Experimental section

### 2.1. Chemicals and materials

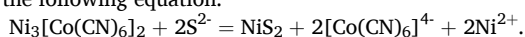
Nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O), potassium cobalticyanide(III) (K<sub>3</sub>[Co(CN)<sub>6</sub>]), sodium citrate trisodium (C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>Na<sub>3</sub>), sodium sulfide (Na<sub>2</sub>S), sodium hydroxide (NaOH), sodium borohydride (NaBH<sub>4</sub>), sodium hydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.7%), and ammonia (NH<sub>3</sub>•H<sub>2</sub>O, 25%) were purchased from Sigma-Aldrich. Commercial ruthenium dioxide (RuO<sub>2</sub>) catalyst was purchased from Johnson Matthey Corporation. All the chemicals mentioned above were of analytical grade and have not been further purified before use.

### 2.2. Synthesis of 100 nm NiCo PBA nanocube

The NiCo PBA were fabricated on the basis of previous reported work [44] with a slight change. In order to downsize the NiCo PBA under 100 nm region, the reaction temperature was decreased to 0 °C for slowing down the crystal growth rate. Typically, 87.2 mg of Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, 132.4 mg of C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>Na<sub>3</sub> and 10 mL of distilled (DI) water were mixed together under ultrasound for 5 min to serve as solution I. Meanwhile, 66 mg of K<sub>3</sub>[Co(CN)<sub>6</sub>] and 10 mL of DI water were mixed together under ultrasound for 5 min to serve as solution II. Subsequently, solution I and solution II were quickly mixed up and underwent continuous aging for 4 h in the ice-water bath of 0 °C under continuous stirring. Finally, the resultant blue sediments were filtered by centrifugation and washed with ethanol for three times, and dried in an oven at 60 °C.

### 2.3. Synthesis of NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes

An inexhaustive anion etching by S<sup>2-</sup> was served to transform NiCo PBA nanocube into NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes according to the following equation:



For a typically synthesis, 20 mg of fresh-made NiCo PBA nanocube and 15 mg of Na<sub>2</sub>S were uniformly dispersed in a mixture of 16 mL of DI water and 16 mL of ethanol. After ultrasound for 5 min, the mixture was continuous stirring in a bain-marle at 60 °C. Precisely, the reaction was shut down at 1 h to obtain the NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes. Then the products were collected by centrifugation and washed with DI water and ethanol for three times, and dried in an oven at 60 °C.

### 2.4. Synthesis of NiCo PBA cross

Typically, 10 mg of the above NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes and 5 mL of NH<sub>3</sub>•H<sub>2</sub>O were dispersed in 40 mL of DI water. After ultrasound for 5 min, the resultant solution was continuous stirring for 1 h in a bain-marle at 60 °C. Then the products were collected by centrifugation and washed with DI water and ethanol for three times, and dried in an oven at 60 °C.

### 2.5. Synthesis of NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> concave hetero-cages (CHCs)

An anisotropic anion etching by OH<sup>-</sup> was served to transform NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes into NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs according to the following equation: Ni<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> + 6OH<sup>-</sup> → 3Ni(OH)<sub>2</sub> + [Co(CN)<sub>6</sub>]<sup>3-</sup>, meanwhile a small amount of dissociative Co<sup>3+</sup> could couple into the Ni(OH)<sub>2</sub> to form the NiCo(OH)<sub>2</sub>. For a typically synthesis, 10 mg of the NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes and 5 mg of NaOH were dispersed in 40 mL of DI water. After ultrasound for 5 min, the resultant solution was continuous stirring for 1 h in a bain-marle at 60 °C. Then the products were collected by centrifugation and washed with DI water and ethanol for three times, and dried in an oven at 60 °C to obtain the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs.

### 2.6. Synthesis of NiCoB/NiS<sub>2</sub> CHCs

The protocol was similar to that of the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs, except that the NaOH was replaced by NaBH<sub>4</sub>. Detailedly, 10 mg of the NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes and 5 mg of NaBH<sub>4</sub> were dispersed in 40 mL of DI water. After ultrasound for 5 min, the mixed solution was continuous stirring for 1 h in a bain-marle at 60 °C. Then the products were collected by centrifugation and washed with DI water and ethanol for three times, and dried in an oven at 60 °C.

### 2.7. Synthesis of NiCoP/NiS cross@frame heterocubes

The protocol was similar to that of the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs, except that the NaOH was replaced by NaH<sub>2</sub>PO<sub>2</sub>. Detailedly, 10 mg of the NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes and 5 mg of NaH<sub>2</sub>PO<sub>2</sub> were dispersed in 40 mL of DI water. After ultrasound for 5 min, the mixed solution was continuous stirring for 1 h in a bain-marle at 60 °C. Then the products were collected by centrifugation and washed with DI water and ethanol for three times, and dried in an oven at 60 °C.

### 2.8. Density functional theory (DFT) calculations

We have employed the VASP package [45] to perform all the spin-polarized DFT calculations within the generalized gradient approximation (GGA) using the PBE formulation. We have chosen the projected augmented wave (PAW) potentials [46,47] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.2 eV. A single gamma-point was used for the Brillouin-zone integration. The electronic energy was considered self-consistent when the energy change was smaller than 10<sup>-5</sup> eV. A geometry optimization was considered convergent until the forces on all atoms were smaller than 0.02 eV/Å.

The surface slab modules were build based on the NiCo PBA cell

structure with the lattice constants of  $a = b = c = 9.8537 \text{ \AA}$  and  $\alpha = \beta = \gamma = 90^\circ$ . The number of atomic layers for (111) (110) and (100) surface slabs were 13, 10 and 10, respectively. The size of (111) (110) and (100) surface slabs were  $13.9135 \text{ \AA} \times 13.9135 \text{ \AA}$ ,  $9.8383 \text{ \AA} \times 13.9135 \text{ \AA}$  and  $9.8383 \text{ \AA} \times 9.8383 \text{ \AA}$ , respectively. The slabs were separated by a  $15 \text{ \AA}$  vacuum layer in the  $z$  direction between the slab and its periodic images. During structural optimizations of the surface models, the bottom 4 at. layers were fixed. The adsorption energy ( $E_{\text{ads}}$ ) of an adsorbate A was defined as:

$$E_{\text{ads}} = E_{\text{A/surf}} - E_{\text{surf}} - E_{\text{A}}$$

where  $E_{\text{A/surf}}$ ,  $E_{\text{surf}}$  and  $E_{\text{A}}$  refers to the energy of A adsorbed on the surface, the energy of the clean surface, and the energy of A in a  $10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$  box, respectively.

## 2.9. Characterizations

Scanning electron microscopy (SEM) images were performed on Hitachi S4800 at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were acquired on a JEOL JEM-2100F transmission electron microscopy manipulated with an accelerating voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images were acquired on a JEM ARM 200 F microscope operated at 200 kV, which provided a nominal resolution of 0.078 nm. The as-tested nanocrystal dispersions were drop-casted on the thin carbon film and dried under ambient conditions. The X-ray absorption fine structure (XAFS) spectra were measured at the beamline BL14W1 station of the Shanghai Synchrotron Radiation Facility, China. The collected EXAFS data were analyzed using the ATHENA program as implemented in the IFEFFIT software packages according to the standard procedures. The wide-angle X-ray powder diffraction (XRD) patterns were performed on a Model D/MAX-RC X-Ray diffractometer with a  $\text{Cu K}\alpha$  radiation. X-ray photoelectron spectrometer (XPS) were performed by using a Thermo VG Scientific ESCALAB 250 spectrometer with an  $\text{Al K}\alpha$  radiator.

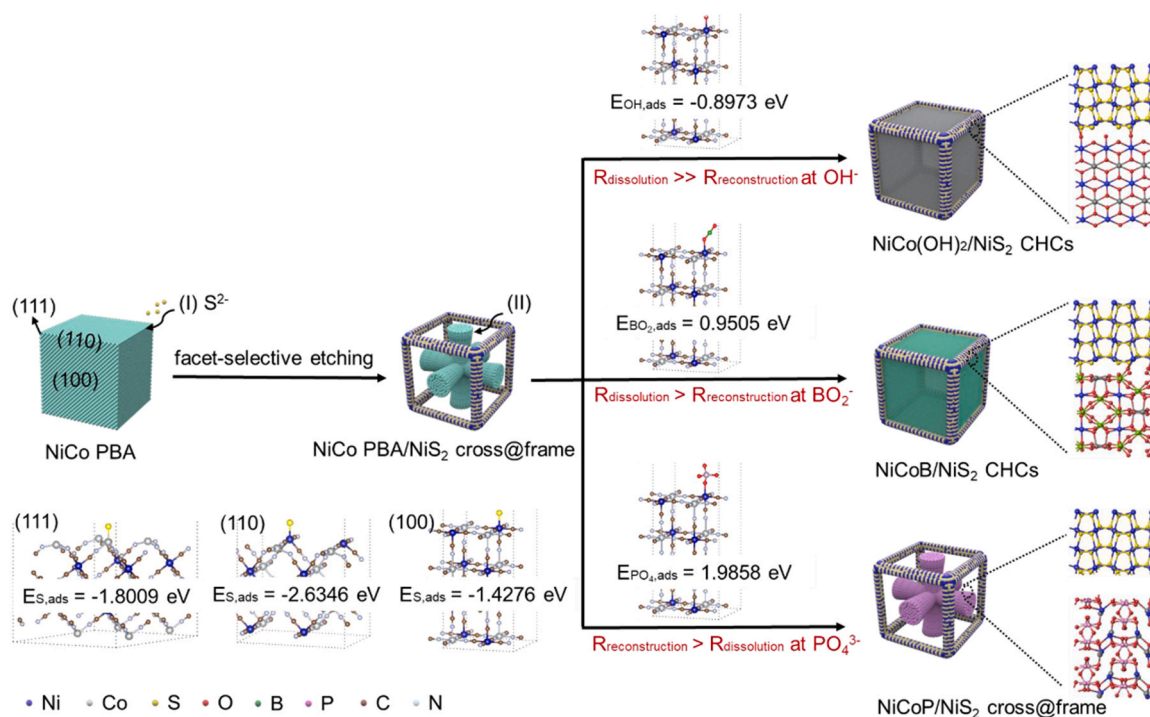
## 2.10. Electrochemical measurements

All the electrochemical measurements were evaluated on a CHI 760E electrochemical analyzer at room temperature. The OER tests were evaluated in 1.0 M KOH electrolyte by employing a three-electrode configuration, including a glassy carbon electrode (GCE, surface area  $0.07 \text{ cm}^2$ ) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite rod as the auxiliary electrode. Potentials in this work were calibrated with respect to reversible hydrogen electrode (RHE) by using the following conversion equation:  $E(\text{RHE}) = E(\text{SCE}) + 0.0591 \text{ pH} + 0.242$ . The as-tested catalyst ink was prepared by dispersing 2 mg of catalyst in 0.7 mL of DI water and 0.3 mL of ethanol solution. After unremitting ultrasound for 20 min,  $10 \mu\text{L}$  of the suspension was pipetted onto the surface of polished GCE by a micro-pipettor and then dried at  $40^\circ\text{C}$ . Finally,  $3 \mu\text{L}$  of Nafion (5 wt%, Sigma-Aldrich) was dropped on the surface of catalyst-modified GCE and dried again. The linear sweep voltammetry (LSV) were conducted in  $\text{N}_2$ -saturated 1.0 M KOH solution at a scan rate of  $5 \text{ mV s}^{-1}$  without ohmic potential drop ( $IR$ ) correction. The chronopotentiometry measurement was tested for 12 h at an overpotential of 340 mV.

## 3. Results and discussion

### 3.1. Kinetic mechanism for the formation of $\text{NiCo}(\text{OH})_2/\text{NiS}_2$ CHCs

The schematic illustration for the formation of  $\text{NiCo}(\text{OH})_2/\text{NiS}_2$  CHCs is elucidated in Fig. 1. The  $\text{fcc}$ -structured  $\text{NiCo}$  PBA nanocubes ( $\text{Ni}_3[\text{Co}(\text{CN})_6]_2$ , a typical MOF) with a side length of 100 nm was served as seed for the two-step anion etching, as the structural features shown in Fig. S1 [48]. Then an incomplete anion etching by  $\text{S}^{2-}$  ions preferentially took place on the edges and corners to form the  $\text{NiCo}$  PBA/ $\text{NiS}_2$  cross@frame heterocubes (step i). DFT calculation systematically investigates the adsorption behavior of  $\text{S}^{2-}$  on (110), (111), and (100) facets of  $\text{NiCo}$  PBA, respectively. The adsorption strength follows the order of edges > corners > planes ( $-2.63 \text{ eV}$  vs.  $-1.80 \text{ eV}$  vs.  $-1.43 \text{ eV}$ ). Accordingly, the etching of  $\text{S}^{2-}$  preferentially started from the



**Fig. 1.** Schematic illustration showing the formation of  $\text{NiCo}(\text{OH})_2/\text{NiS}_2$  CHCs and the proposed etching mechanism from DFT calculations. Step I: facets-selective etching by  $\text{S}^{2-}$ . Step II: kinetics-controlled etching by  $\text{OH}^-$ ,  $\text{BO}_2^-$ ,  $\text{PO}_4^{3-}$ , respectively.

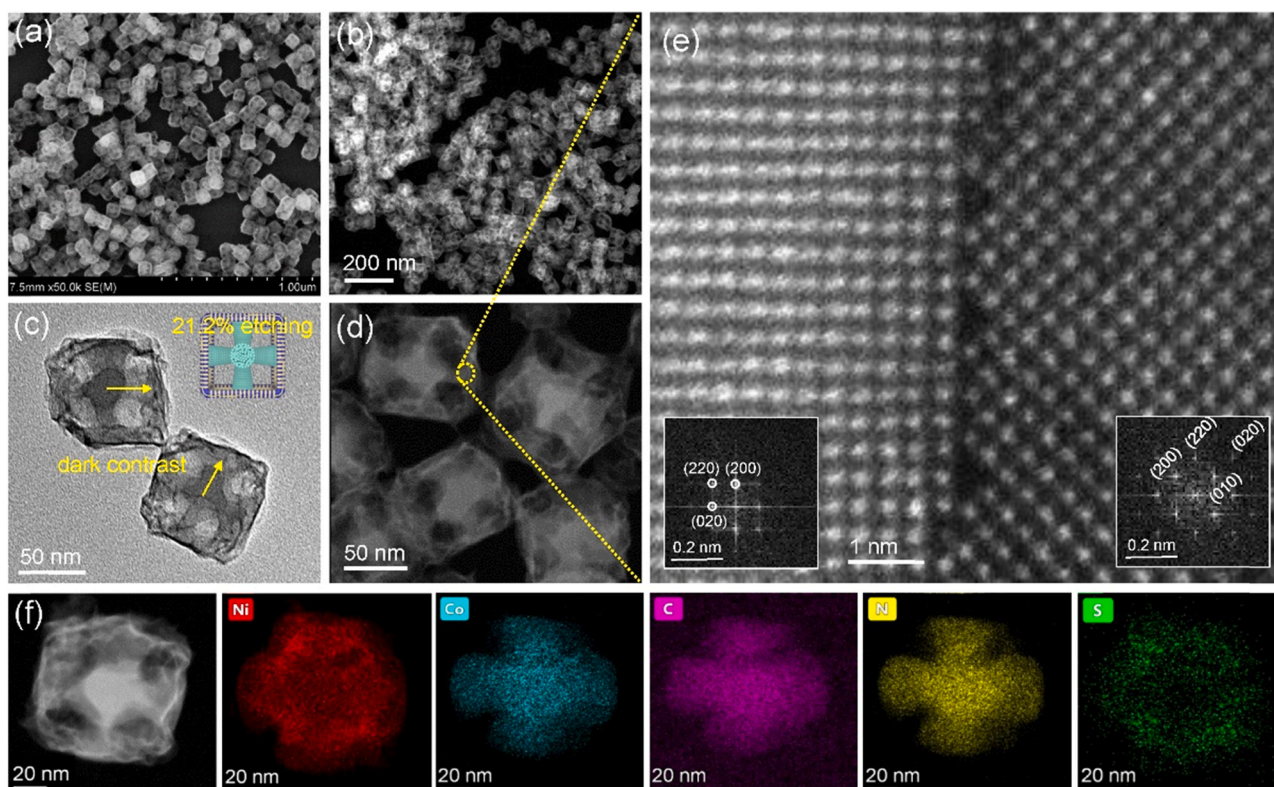


edges/corners and the etching rate tended to be faster along the body diagonal direction of the cubes, thus forming an ultrathin  $\text{NiS}_2$  frame externally, leaving the internally residual PBA with eight-corners-cutted cross-like structure. Following that, the internal PBA cross underwent second anion etching by  $\text{OH}^-$  to form  $\text{NiCo}(\text{OH})_2/\text{NiS}_2$  CHCs, or form the  $\text{NiCoB}/\text{NiS}_2$  CHCs by  $\text{BO}_2^-$ , and form the  $\text{NiCoP}$  cross@ $\text{NiS}_2$  frame by  $\text{PO}_4^{3-}$  (step ii). It is worth noting that the theoretical solubility product ( $K_{\text{sp}}$ ) of secondary etching product must be larger than  $\text{NiS}_2$  [49]. In this way, the secondary etchant ( $\text{OH}^-$ ,  $\text{BO}_2^-$ ,  $\text{PO}_4^{3-}$ ) is unable to replace the  $\text{S}^{2-}$  in the solid phase based on solubility equilibrium, thus avoid the excessive corrosion of as-formed  $\text{NiS}_2$  frame. The distinctive shape of final products is attribute to the difference of kinetical dissolution and reconstitution rates induced by  $\text{OH}^-$ ,  $\text{BO}_2^-$ , and  $\text{PO}_4^{3-}$  on PBA cross, where the adsorption energy follows the order of  $\text{OH}^- > \text{BO}_2^- > \text{PO}_4^{3-}$  (−0.8973 eV vs. 0.9505 eV vs. 1.9858 eV). Obviously, the  $\text{OH}^-$  and  $\text{BO}_2^-$  show stronger adsorption energy relative to  $\text{PO}_4^{3-}$ , which could weaken the relative strength of the interior chemical bonds in PBA cross, thus leading to the decrease of the reaction activation energy of PBA dissolution. In this condition, the metal/organic linkers of NiCo PBA cross were quickly dissolved and then the dissociative Ni, Co,  $\text{OH}^-$  were confined in the  $\text{NiS}_2$  frame to take reconstitution, thus forming the  $\text{NiCo}(\text{OH})_2/\text{NiS}_2$  CHCs ( $R_{\text{dissolution}} \gg R_{\text{reconstitution}}$ ), or  $\text{NiCoB}/\text{NiS}_2$  CHCs ( $R_{\text{dissolution}} > R_{\text{reconstitution}}$ ). In contrast, the week adsorption of  $\text{PO}_4^{3-}$  on NiCo cross led to a slow kinetic dissolution rate, thus balanced the  $R_{\text{dissolution}}$  and  $R_{\text{reconstitution}}$  to gently convert NiCo PBA into NiCoP with cross-like structure remained ( $R_{\text{reconstitution}} > R_{\text{dissolution}}$ ).

### 3.2. Characteristics of $\text{NiCo}(\text{OH})_2/\text{NiS}_2$ CHCs

The intermediate products induced by  $\text{S}^{2-}$  etching were collected at different reaction time to show the detailed morphologic evolution (Fig. S2). It displays the etching process started from the edges and corners of NiCo PBA cube, which is basically consistent with the

speculation of DFT calculation. The structural characterization of NiCo PBA/ $\text{NiS}_2$  cross@frame heterocubes is investigated by large-scale SEM image (Fig. 2a) and HAADF-STEM image (Fig. 2b). It displays four distinct voids within a square border, indicating the possible formation of cross@frame structure. The wall thickness of external  $\text{NiS}_2$  frame was measured to be 16.2 nm (Fig. S3), which is much thinner than most of previously reported frame/cage structures (Table S1). It indicates the ultrathin feature of the NiCo PBA/ $\text{NiS}_2$  cross@frame heterocubes derived from the partly etching of PBA cube. The internal cross-like structure is confirmed by etching the external  $\text{NiS}_2$  framework. As shown in Fig. S4, the typical concave cross shape could be observed with eight corners cutted down. HRTEM images demonstrate obvious light and shade contrast along the center to edge (marked by yellow arrows), further confirming the existence of internal cross structure based on the difference in depth of field (Figs. 2c and S5). By measuring the side length (~90 nm) and diameter of void (~28.5 nm) of NiCo PBA/ $\text{NiS}_2$  cross@frame heterocubes, the etching ratio of  $\text{S}^{2-}$  was determined to be 21.2%. The interplanar spacing was measured to be 0.206 nm at the edges and 0.236 nm at the cross, corresponding to the (110) facets of *fcc*- $\text{NiS}_2$  and (331) facets of *fcc*-NiCo PBA, respectively (Fig. S5c). HAADF-STEM image shows the lattice boundary and atomic arrangement along the imageable junction of  $\text{NiS}_2$  frame and NiCo PBA cross (Fig. 2d, e). Distinct atom arrangement mode with vacancies/defects could be observed along the boundary, indicative the compositional heterogeneity between the frame and cross. Elemental mapping indicates the outermost distribution of S with a hollow cubic shape, the entire distribution of Ni with a cubic porous shape, and the inner distribution of Co, N and C with a cross shape (Fig. 2f). Such observation points to explicit spatial distribution of inner NiCo PBA cross and epibolic  $\text{NiS}_2$  frame, well matching the heterogeneous composition distribution between cross and frame. XRD pattern was performed to investigate the crystal structure of NiCo PBA/ $\text{NiS}_2$  cross@frame (Fig. S6). It combines the characteristic peak of both the NiCo PBA (JCPDS no. 89-3738) and



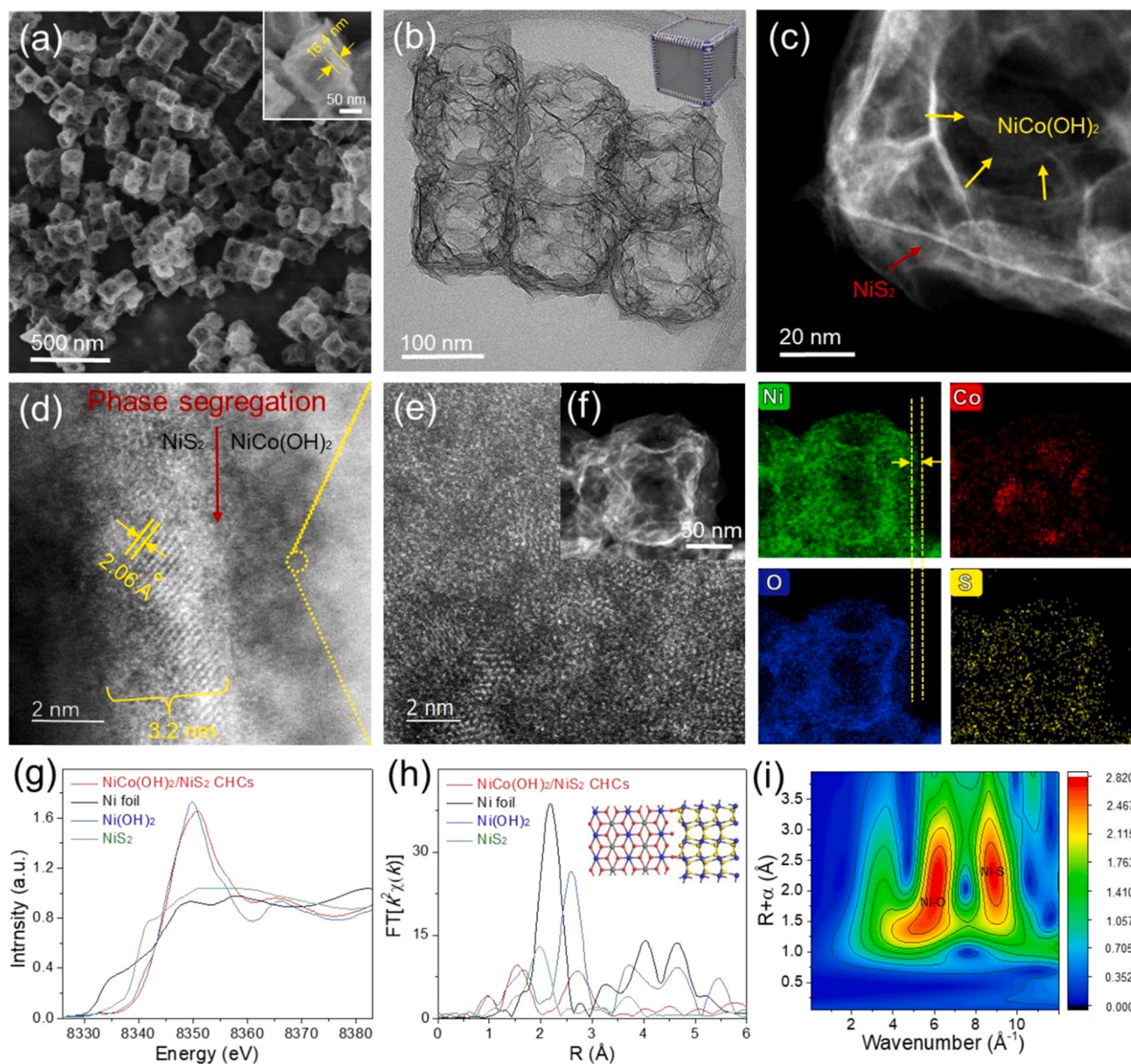
**Fig. 2.** Characteristics of NiCo PBA/ $\text{NiS}_2$  cross@frame heterocubes. (a) SEM image. (b) Large scale HAADF-STEM image. (c) HRTEM image. (d-e) HAADF-STEM image, insert: corresponding FFT patterns. (f) EDS elemental mapping images.



NiS<sub>2</sub> (JCPDS no. 80-0376). XPS demonstrates the existence of Ni, Co, S, C, and N in NiCo PBA/NiS<sub>2</sub> cross@frame (Fig. S7). Detailedly, the characteristic peak of Ni 2p is located at 855.4 eV (2p<sub>3/2</sub>) and 873.1 eV (2p<sub>1/2</sub>), corresponding to +2 state of Ni in Ni-S and Ni-N. The characteristic peak of Co 2p is located at 781.2 eV (2p<sub>3/2</sub>) and 796.2 eV (2p<sub>1/2</sub>), indicating +3 state in Co-N. The S 2p spectrum reveals two distinct peaks at 161.6 eV (2p<sub>3/2</sub>) and 162.7 eV (2p<sub>1/2</sub>), demonstrating the presence of S<sup>2-</sup> ions. The main characteristic peak of C 1s and N 1s is located at 284.5 eV and 397.8 eV, respectively, verify the bonding of C≡N. All above results confirm the formation of NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes, which is originated from selectively and partly carving of NiCo PBA cube.

The secondary anion etching by OH<sup>-</sup> is served to convert NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes into NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs. As shown in Fig. 3a, SEM image of the products shows a concave structure with cubic configuration. It indicates the disappearance of internal NiCo PBA cross

and the preservation of external NiS<sub>2</sub> frame after OH<sup>-</sup> etching. Meanwhile, the wall thickness of outer frameworks was measured to be ca. 16.4 nm, basically consisted with that of the NiCo PBA/NiS<sub>2</sub> cross@frame heterocubes, indicating the robustness of NiS<sub>2</sub> frame after introducing the OH<sup>-</sup> (insert). HRTEM image shown in Fig. 3b displays a cage-like nanostructures consisted of hierarchical flexible nanosheets, which is typical morphology characteristic of the layered hydroxide. HAADF-STEM image is provided to shows the fine structure of NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs (Fig. 3c). Due to the well-defined dark contrast, where the NiS<sub>2</sub> refers to a bright straight line and the NiCo(OH)<sub>2</sub> refers to dim hierarchical flexible region, the existence of sulfide/hydroxide hetero-interface could be confirmed. Fig. 3d clarify the distinctive atomic arrangement in NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs, that the NiS<sub>2</sub> possesses highly ordered atom arrangement with consistent lattice orientation and well spatial alignment, while the NiCo(OH)<sub>2</sub> part displays highly disordered lattice orientations with anisotropy (Fig. 3e). This result further

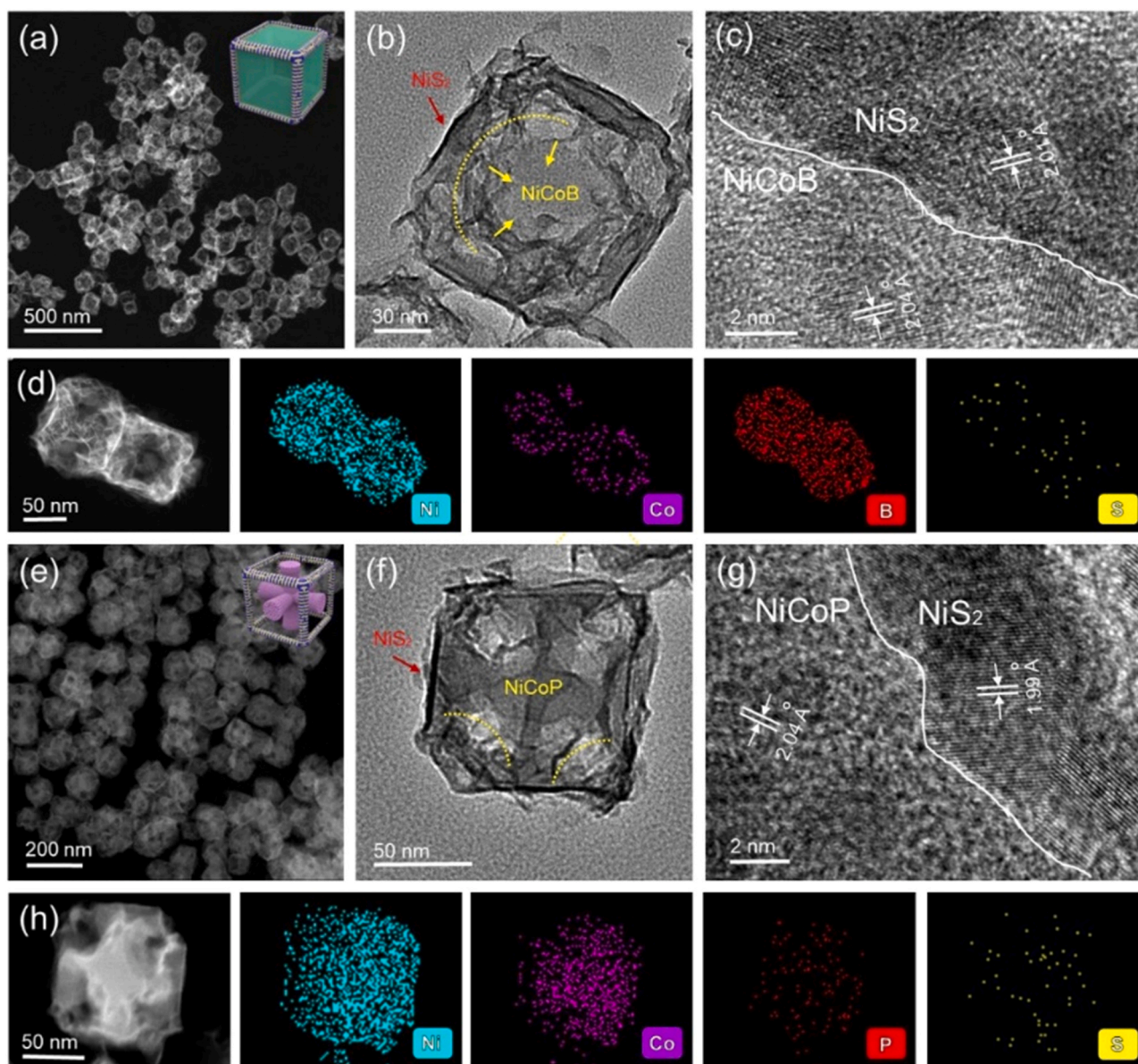


**Fig. 3.** Characteristics of NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs. (a) SEM image. (b) HRTEM image. (c-e) HAADF-STEM images. (f) EDS elemental mapping images. (g) Ni K-edge XANES spectra. (h) EXAFS spectra. (i) WT-EXAFS.

confirms the existence of heterointerface consisted of sulfide and hydroxide. Element mapping shows the existence of Ni, O, and S element across the entire concave cages, along with the existence of less Co inside (Fig. 3f). It confirms the successfully hydroxylation to generate the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs with compositional heterogeneity. XRD pattern of NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs shows newly emerged characteristic peaks at 33.8, 37.7, and 59.9° (refer to (100), (101), (110) facets of hydroxide) and reserved characteristic peaks at 28.2, 39.9, and 59.9° (NiS<sub>2</sub>, JCPDS no. 80-0376) compare to those of the NiCo PBA/NiS<sub>2</sub> cross@frame (Fig. S8). It indicates the composition variation after OH<sup>-</sup> etching. Fig. S9 shows the XPS survey of the NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs, which displays similar electronic structure and valence state at Ni 2p, Co 2p, and S 1s regions compare to those of the NiCo PBA/NiS<sub>2</sub> cross@frame. Nevertheless, the O 1s spectrum is deconvoluted into three peaks at 530.4, 531.6, 533.1 eV, corresponding to the lattice oxygen, substituted hydroxyl group, and surface oxygen, respectively, suggesting the formation of hydroxide states.

The Ni K edge XAFS spectroscopy was measured to probe the localized electronic structure and coordination environment in NiCo(OH)<sub>2</sub>/

NiS<sub>2</sub> CHCs (Fig. 3g). Obviously, both the pre-edge and K edge position upshift to higher energy values, indicative the reduced electron density around the 3d orbital of Ni sites. It demonstrates the ability of NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs to shuttle the electrons away, thus creating higher-valence-state Ni species. This result also indicates the increased disorder of localized Ni sites compare to bulk NiS<sub>2</sub> and Ni(OH)<sub>2</sub>, which could be originated from the chronological interaction of S<sup>2-</sup> and OH<sup>-</sup> that induce the rearrangement of electron distribution. The Ni EXAFS demonstrates two prominent peaks at 1.56 Å and 2.70 Å, indicating the variation of coordination environment induced by spectra sulfide and hydroxide (Figs. 3h and S10). Meanwhile, the wavelet transform (WT) contour plot demonstrates maximum intensity at two distinctive areas ( $k = 6.0 \text{ Å}^{-1}$  refers to Ni-O,  $k = 8.8 \text{ Å}^{-1}$  refers to Ni-S), confirming the heterogeneous phase distribution in NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs (Fig. 3i). Table S2 shows the coordination number (CN) of Ni-O ( $5.9 \pm 0.5$ ) and Ni-S ( $1.4 \pm 0.6$ ), which is much lower than bulk Ni(OH)<sub>2</sub> and NiS<sub>2</sub>, respectively. It demonstrates a disordered local coordination induced by defects, vacancies from heterointerface [50]. Meanwhile, the average bond length of Ni-O and Ni-S was measured to be  $2.03 \pm 0.01$  and



**Fig. 4.** (a) HAADF-STEM image, (b-c) HRTEM images, (d) EDX element mapping images of NiCoB/NiS<sub>2</sub> CHCs. (e) HAADF-STEM image, (f-g) HRTEM images, (h) EDX element mapping images of NiCoP/NiS<sub>2</sub> cross@frame heterocubes.



$2.48 \pm 0.01 \text{ \AA}$ , respectively. Such longer bond distance of Ni-S indicates the existence of lattice strain exerted on crystal lattice of  $\text{NiS}_2$  frame, which could be arisen from secondary anion etching of  $\text{OH}^-$  that causes hybridization and electron transfer into Ni d orbitals [51]. Therefore, above results manifest the successful formation of  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs and also indicate the establishment of increased lattice chaos, strong lattice strain induced by heterogeneous interface, and the reduced electron density around Ni 3d orbital.

### 3.3. Universal strategy generalized to the formation of $\text{NiCoB}/\text{NiS}_2$ and $\text{NiCoP}/\text{NiS}_2$

The secondary anion etchant could be generalized to  $\text{BH}_4^-$  or  $\text{H}_2\text{PO}_4^-$  for constructing sulfide/boride or sulfide/phosphide heterogeneous combinations. Fig. 4a–d demonstrates the structural feature of  $\text{NiCoB}/\text{NiS}_2$  CHCs. Both the SEM and HRTEM images display a cage-like structure with the disappearance of internal NiCo PBA cross, which are similar to that of the  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs. The wall thickness of outer frameworks was measured to be ca. 16.5 nm, indicative the ultrathin feature of  $\text{NiCoB}/\text{NiS}_2$  CHCs. The interplanar spacing was measured to be 2.01 nm at the frame and 2.04 nm at the cage, corresponding to (110) facets of  $\text{NiS}_2$  and (211) facets of  $\text{NiCoB}$ , respectively. Element mapping verifies the existence of Ni, Co, B, and S element in  $\text{NiCoB}/\text{NiS}_2$  CHCs, confirming the formation of  $\text{NiCoB}$  compound and the well reservation of  $\text{NiS}_2$  parts. However, XRD pattern of the  $\text{NiCoB}/\text{NiS}_2$  CHCs only displays the characteristic peaks of  $\text{NiS}_2$  (JCPDS no. 80-0376), that no obvious characteristic peaks of  $\text{NiCoB}$  could be observed (Fig. S11). This result could be possibly due to relative low crystallinity degree of  $\text{NiCoB}$  [52]. XPS survey demonstrates the existence of Ni, Co, B, and S element in  $\text{NiCoB}/\text{NiS}_2$  CHCs (Fig. S12). The formation of meta-boron is evidenced by high resolution B 1s spectrum, which displays typical character peak of M-B (187.8 eV), accompanied by B-O peaks (191.7 eV, 192.5 eV). Nevertheless, both the characteristic peak at Ni 2p, Co 2p region negatively shift  $\sim 0.3 \text{ eV}$  as compare to those of  $\text{NiCo PBA}/\text{NiS}_2$  cross@frame, indicating that the electronic structure of  $\text{NiCoB}/\text{NiS}_2$  CHCs could be tuned by boronizing [53,54].

Fig. 4e–h demonstrates the structural feature of  $\text{NiCoP}/\text{NiS}_2$  cross@frame, which was prepared by secondary anion etching of  $\text{H}_2\text{PO}_4^-$ . The products display a typical cross@frame structure with four distinct voids, which are similar to that of the  $\text{NiCo PBA}/\text{NiS}_2$  cross@frame. Meanwhile, the wall thickness of external  $\text{NiS}_2$  frame was measured to be 16.3 nm, basically constant with that of the  $\text{NiCo PBA}/\text{NiS}_2$  cross@frame. The interplanar spacing was measured to be 0.199 nm at the frame and 0.204 nm at the cross, corresponding to the (110) facets of *fcc*- $\text{NiS}_2$  and (201) facets of *fcc*-NiP, respectively. Elemental NiCo PBA/ $\text{NiS}_2$  cross@frame mapping images confirm the existence of Ni, Co, P, and S element, confirming the successful phosphating in  $\text{NiCo PBA}/\text{NiS}_2$  cross@frame to form the  $\text{NiCoP}$  compound. Meanwhile, the  $\text{NiS}_2$  parts could be partly retained to construct hetero-interface with newly-formed  $\text{NiCoP}$ . The compositional heterogeneity of  $\text{NiCoP}/\text{NiS}_2$  cross@frame is confirmed by XRD pattern (Fig. S13). It combines the characteristic peak of both the NiP (JCPDS no. 03-0953, showing a slight shift due to the incorporation of Co) and  $\text{NiS}_2$  (JCPDS no. 80-0376). XPS survey demonstrates the co-existence of Ni, Co, P, S element in  $\text{NiCoP}/\text{NiS}_2$  cross@frame (Fig. S14). Specifically, the formation of meta-phosphorus is evidenced by the high resolution P 2p spectrum, which displays character peaks at 129.4, 130.5, and 132.7 eV, correspond to the P  $2p_{3/2}$ , P  $2p_{1/2}$ , and P-O species, respectively. Notably, both the characteristic peaks at Ni 2p, Co 2p region show the negatively shift of ca. 0.3 eV, which could be derived from the electronic interactions induced by phosphorization. All above results confirm the formation of  $\text{NiCoB}/\text{NiS}_2$  CHCs (or  $\text{NiCoP}/\text{NiS}_2$  cross@frame) by subsequent B/P etching, which proves the feasibility of stepwise anion etching method for generating well-structured heterogeneous superstructures.

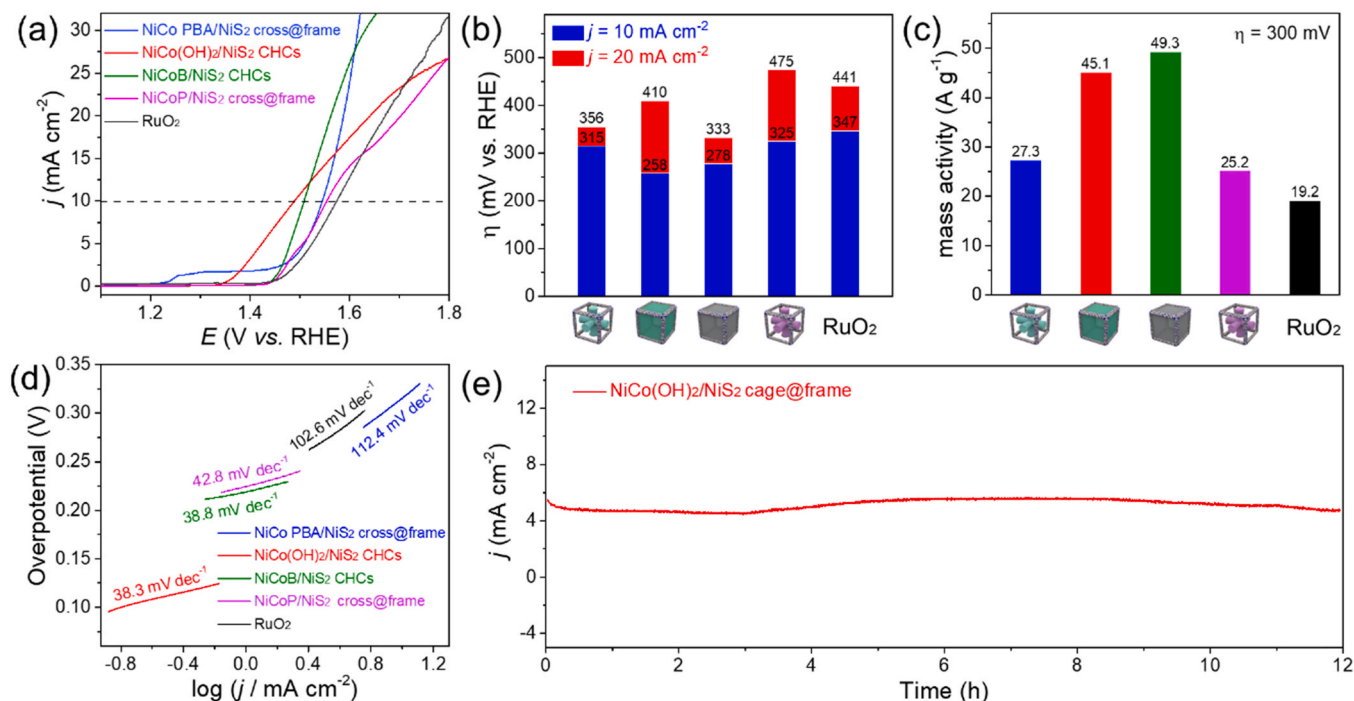
### 3.4. OER performance of the $\text{NiCo(OH)}_2/\text{NiS}_2$ CHCs

As a proof-of-concept application, the electro-catalytic performance of  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs was investigated by OER in 1 M KOH electrolyte. As the polarization curves displayed in Fig. 5a, the  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs exhibit the lowest overpotential of 258 mV to achieve the current density of  $10 \text{ mA cm}^{-2}$ , while the  $\text{NiCo PBA}/\text{NiS}_2$  cross@frame,  $\text{NiCoB}/\text{NiS}_2$  CHCs,  $\text{NiCoP}/\text{NiS}_2$  cross@frame, and  $\text{RuO}_2$  requires larger overpotential of 315 mV, 278 mV, 325 mV, and 347 mV, respectively. Moreover, the  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs still maintain the superior overpotential at a current density of  $20 \text{ mA cm}^{-2}$  (Fig. 5b) and afford highest mass activity at an overpotential of 300 mV (Fig. 5c), indicative the maximum catalytic output at minimized overpotentials. The corresponding Tafel plots shown in Fig. 5d implies that  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs exhibit an ultra-small Tafel slope of  $38.3 \text{ mV dec}^{-1}$ , which is much lower than that of the  $\text{NiCo PBA}/\text{NiS}_2$  cross@frame ( $112.4 \text{ mV dec}^{-1}$ ),  $\text{NiCoB}/\text{NiS}_2$  CHCs ( $38.8 \text{ mV dec}^{-1}$ ),  $\text{NiCoP}/\text{NiS}_2$  cross@frame ( $42.8 \text{ mV dec}^{-1}$ ) and  $\text{RuO}_2$  ( $102.6 \text{ mV dec}^{-1}$ ), indicating the favorable OER kinetics over the  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs. Above results reveal that the products after secondary anion etching ( $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs,  $\text{NiCoB}/\text{NiS}_2$  CHCs, and  $\text{NiCoP}/\text{NiS}_2$  cross@frame) show better OER kinetics than that of the  $\text{NiCo PBA}/\text{NiS}_2$  cross@frame. It is because (i) after the secondary etching, the residual PBA cross with low activity was transformed into hydroxide/phosphide/boride component, which hold better intrinsic activity for OER [55,56]; (ii) as investigated by EXAFS, the newly formed sulfide/hydroxides heterointerface could induce the synergistic effects of lattice strain, electronic regulation, and interface engineering. These factors are beneficial for enhancing the catalytic activity [57]. The OER performance of  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs is also compared with formerly reported noble-metal-free electro-catalysts in alkaline media (Table S3), which exceeds most of them to further confirming its optimal overpotential and Tafel slope. Chronoamperometry measurement was carried out to verify the long-term durability of  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs. Impressively, the  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs could maintain the current attenuation continuous operation at 1.57 V for 12 h with 13.8% potential decrease, surpass the other four catalysts (Fig. S15). TEM characterization (Fig. S16) reveals that the concave and hollow structure of the  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs could be well maintained after chronoamperometry measurement. In addition, TEM images of  $\text{NiCoB}/\text{NiS}_2$  CHCs and  $\text{NiCoP}/\text{NiS}_2$  cross@frame after chronoamperometry measurement show that the basic structures could be maintained, indicating the well structural robustness of the products after secondary anion etching (Fig. S17). Above results testify the superior OER activity and stability of  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs, which could be attributed to the following reasons. (i) The  $\text{NiS}_2$  presented on frameworks is born with high activity and superior electrical conductivity, meanwhile the  $\text{NiCo(OH)}_2$  presented on inner cages endows OER-favored species with straightway conversion efficiency [58]. (ii) The use of  $\text{NiCo PBA}$  under sub-100 nm, the fractional etching by  $\text{S}^{2-}$  (21.2%), and the additive free of metal cation source endows  $\text{NiCo(OH)}_2/\text{NiS}_2$  CHCs with ultrathin walls (16.2 nm), which could offer higher surface-area-to-volume ratio and accelerate the gas diffusion, electrolyte transfer, and reactants transportation during OER. (iii) The concave structure not only affords high density of atomic steps/kinks to favor the exposure of active sites, but also maintains structural stability because the internal cage can serve as inner skeleton to support the outer frame [59]. (iiii) The strongly coupled sulfide/hydroxides heterointerface could induce the synergistic effects of lattice strain, electronic regulation, and interface engineering.[60].

## 4. Conclusions

In summary, we establish a novel synthetic concept to generate a series of heterostructures (*i.e.*  $\text{NiCo(OH)}_2/\text{NiS}_2$ ,  $\text{NiCoB}/\text{NiS}_2$   $\text{NiCoP}/\text{NiS}_2$  with well-defined geometrical configuration (concave, cross@frame). The kinetical formation mechanism involves: (i) insufficient anion





**Fig. 5.** OER performance of NiCo(OH)<sub>2</sub>/NiS<sub>2</sub> CHCs and controllable samples in 1 M KOH electrolyte with mass loading of 0.27 mg cm<sup>-2</sup>. (a) LSV polarization curves. (b) Overpotentials at current density of 10 and 20 mA cm<sup>-2</sup>. (c) Mass activity at η = 300 mV. (d) Tafel plots. (e) Chronoamperometric response at an overpotential of 340 mV.

etching by S<sup>2-</sup> preferentially on edges and corners; (ii) secondary anion etching on internal PBA cross, where the dissolution and reconstitution kinetics are manipulated to determine the final shape. Such design tends to generate strongly coupled heterointerface with hollow, concave, and ultrathin features, which could induce lattice strain, electronic regulation, and interface engineering to boost the OER activity. The two-step and facet-selective anion etching under kinetical control challenges traditional seed-mediated growth to construct well-defined heterogeneous structure, which opens up a new avenue for both fundamental study and realization of various functionalities of non-noble metal nanostructures.

#### CRediT authorship contribution statement

**Jingchun Wang:** Methodology, Investigation, Validation, Writing – original draft, Writing – review & editing. **Anzhou Yang:** Formal analysis, Methodology. **Jiatian Li:** Methodology, Investigation, Conceptualization. **Keying Su:** Investigation, Visualization. **Yawen Tang:** Resources, Funding acquisition. **Xiaoyu Qiu:** Supervision, Writing – review & editing, Project administration.

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#### Declaration of competing interest

The authors declare no conflict of interest.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2021.120727](https://doi.org/10.1016/j.apcatb.2021.120727).

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